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Predicting Movement of Selected Metals in Soil Application to Disposal Problems

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16. ABSTRACT

Data from laboratory column studies of movement of selected metals in Municipal Solid Waste (MSW) leachate through soils from several parts of the U.S. were used as a base for developing simple field-oriented tools for predicting pollutant movement. The metals studied were arsenic, beryllium, cadmium, chromium, copper, iron, mercury, nickel, lead, selenium, vanadium and zinc. Principal variables in the laboratory study and in the models were (a) soil physical/chemical properties such as clay content, pH, and iron/ manganese hydrous oxide content, and, (b) leachate properties such as total organic carbon (TOC) and total salts.

The first model was based on the Lapidus and Amundson (L-A) equation. A simpler, more adaptable model based on the Error Function equation was developed and tested. Predictions for rates of metal movement through soil in municipal solid waste leachates were equally effective by either model but the L-A method of developing the model was somewhat more difficult in terms of amount of input data and parameter estimation.

Work was also conducted on movement in soil of the natural phenolic fraction of MSW leachate and six monohydroxybenzene derivatives of phenol added to MSW leachate. Movement rates and soil and leachate charcteristics that influences rates were identified; the results have not been incorporated into the model.

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ENVIRONMENTAL RESEARCH BRIEF

Predicting Movement of Selected Metals in Soil: Application to Disposal Problems

Hinton K. Howard*

Abstract

Data from laboratory column studies of movement of selected metals in municipal solid waste (MSW) leachate through soils from several parts of the United States were used as a base for developing simple, field-oriented tools for predicting pollutant movement. The metals studied were arsenic, beryllium, cadmium, chromium, copper, iron, mercury, nickel, lead, selenium, vanadium, and zinc. Principal variables in the laboratory study and in the models were 1. Physical/chemical properties of soil such as clay content, pH, and iron/manganese hydrous oxide content, and 2. Leachate properties such as total organic carbon (TOC) and total salts.

The first model was based on the Lapidus and Amundson (L-A) equation. A simpler, more adaptable model based on the Error Function equation was also developed and tested. Both models effectively predicted rates of metal movement through soil in MSW leachates, but the L-A method of developing the model was somewhat more difficult in terms of the amount of input data and parameter estimation.

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Work was also conducted on movement in soil of the natural phenolic fraction of MSW leachate and of six monohydroxybenzene derivatives of phenol added to MSW leachate. Movement rates and the soil and leachate characteristics that influenced the rates were identified; the results have not been incorporated into the model.

This Research Brief was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research projects that are fully documented in separate reports and journal articles.

Introduction

The composition of landfill leachate and the characteristics/composition of the soil determine the rate at which metals in the leachate migrate through the soil. Having the capability to predict migration rates based on a knowledge of the leachate and soil characteristics would greatly aid in the design of landfills. The first section of this Research Brief outlines the small-scale soil column experiments that measured migration rates of various materials through a variety of soils and the development of equations for predicting leachate migration rates in soils. The work builds on the results of a previous literature survey (1) and laboratory soil column studies with MSW leachate (2,3,4) by Dr. Wallace H. Fuller et al.,

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at the University of Arizona. The second section presents information concerning adsorption and movement in soils of the phenolic fraction of MSW leachate.

No field data were available to test the equations for predicting leachate migration rates. It is thought that models based on laboratory soil column data are capable of making qualitative predictions (relative migration rates, etc.) but are much less accurate for quantitative predictions. The hydraulic characteristics of a laboratory soil column may not be very representative of field conditions because 1. removing a soil sample from the ground and placing it in a column can alter the sample physically and 2. the sample(s) size or numbers may not be sufficient to represent the total ground area of interest. The adsorptive characteristics of a soil sample will, however, represent the field characteristics unless the adsorptive process is slow and the contact times (between leachate and soil) are different in the laboratory than in the field.

Models based on laboratory soil column data may not quantitatively predict migration in field soils. Nevertheless, predictions of extremes based on laboratory data can provide important perspective concerning pollutant migration in the field, e.g., identifying contaminants or soil/leachate conditions that will produce slow or rapid migration.

Soil Column Procedure

The several experiments covered in this publication took place during the period 1976-1982. The same general procedures, as described below, were used for all experiments, with variations introduced as required for specific experiments.

Leachate was generated in 4000-L containers packed with materials representative of those found in municipal waste. After packing, the containers were filled with water and the resulting mix was allowed to age. Leachate was withdrawn from the bottom of the tank anaerobically and stored under a blanket of carbon dioxide. Leachate was spiked with the metals of interest and applied to the 5-cm-diameter x 10-cm-length packed columns using a constant head apparatus that supplied a blanket of carbon dioxide to prevent oxidation/precipitation of leachate components. Leaching through the soils was continued until one of three conditions was met: breakthrough (effluent concentration = influent concentration); steady state (unchanging or very slowly changing effluent concentration); or continued absence of a trace metal after extended leaching. The trace element content of the leachate was determined and used to calculate a correlation matrix and a multiple regression analysis of trace metal mobility versus soil properties.

The soils used in the experiments, obtained from different regions of the United States, exhibited a wide range of composition and characteristics (Table 1). Before being packed into 5-cm-diameter x 10-cm- length columns, the soils were air dried and passed through 0.5-mm screens. Soil columns were perfused with either constant head or constant flux, depending upon the specific experimental objectives.

Metals Migration

The metals used in the soil properties study (5,6) were arsenic, beryllium, cadmium, chromium, copper, mercury, nickel, lead, selenium, vanadium, and zinc. This study investigated the effect of soil properties, leachate properties, and leachate flow rates on Metal Migration.

Soil Properties

There were 11 different soils from 7 orders in the Soil Taxonomy classification system. The best correlation with mobility was obtained for the percent clay in a soil, followed in order by the surface area and the percentage of free iron oxides. The researchers concluded that, even though the mobilities of trace metals differed significantly, qualitatively predicting mobility on the basis of these soil properties should be possible.

Leachate Properties

The leachate properties studies (4,5,7,8) examined the movement of salts of cadmium, iron, nickel, and zinc through six soils (see Table 1). The leachate composition variables were total organic carbon (TOC), total inorganic salts (SALT), and iron (Fe).

Leachate was displaced through the soil under saturated anaerobic conditions at constant flux rates. Influent and effluent analysis at set time intervals provided the basis for conclusions concerning the influence of the various parameters on metal migration.

For each of the four metals in all of the soils it was found that the rate of migration was higher when the concentration of any of the three parameters (TOC, SALT, Fe) was higher. The quantitative results from these studies were used to develop equations for predicting metals migration.

Leachate Flow Rate

In the leachate flow rate studies (9,10), leachates were individually enriched with salts of arsenic, beryllium, cadmium, chromium, iron, nickel, and zinc and displaced through soils under anaerobic saturated conditions with controlled flow rates from 1.2 to 18 cm/day. Nine soils were used. Effluent collected at hourly intervals was analyzed for the metal ions of interest. Solution displacements continued until the concentration of the metal in the effluent equaled that of the influent.

In general, the results showed that the slower the flux, the lower the concentration of metals in the effluent at a given number of pore volume displacements. The magnitude of the effect was large for arsenic, beryllium, chromium, and iron ions; and small for cadmium, nickel and zinc ions.

Prediction Equations

The general method to develop prediction equations (11,12) was regression analysis with the use of movement rates for Ni, Cd, and Zn from the soil column studies. Soil and leachate properties were used to obtain coefficients for the prediction equation.

The predictive equation developed from the error function model was:

$$C/Co = 0.5 \text{ erfc } [(Rz-vt)/(4DRt)^{0.5}] \quad [1]$$

where C is the solute concentration in soil water at time t and depth z; Co is the solute concentration in the input

Table 1. Soil Properties*

Soil Series	Iron Oxide (%)	Clay (%)	Surface (M^2/g)	Dominant Clay Minerals	Texture (USDA)
Davidson	17	52	51	Kaolin. +	Cl.
Molokai	23	52	67	Kaolin., Gibbs.	Cl.
Nicholson	5.6	49	120	Vermic.	Si. Cl.
Fanno	3.7	46	122	Mont., mica	Cl.
Mohave (Ca)	2.5	40	128	Mica, Mont.	Cl. loam
Chalmers	3.1	31	96	Mont., Vermic.	Si Cl loam
Ava	4	31	62	Vermic., Kaolin.	Si Cl loam
Anthony	1.8	15	20	Mont., mica	Sandy loam
Mohave	1.7	11	38	Mica, Kaolin.	Cl. loam
Wagram	0.6	4	8	Kaolin., Chlor.	Loamy sand
Kalkaska	1.8	5	9	Chlor., Kaolin.	Sand

*Most common values cited in the references at the end of this Research Brief.
+Cl -Clay; Si -Silty; Mont. -Montmorillonite; Kaolin.-Kaolnite; Gibbs.-Gibbsite; Chlor.-Chlorite; Vermic.-Vermiculite

solution; z is the depth; t is the time; v is the pore water velocity; R is the retardation factor (dimensionless); D is the diffusion coefficient (units 12/t); and erfc is the complementary error function. The user obtains values for D and R from regression equations [2] of the form:

$$V = C1P1 + C2P2 + C3P3 + \ldots \quad [2]$$

where V is the value for D or R to be used in equation [1]; C1, C2, C3, etc., are coefficients that were developed from regression analysis of the soil column data, and P1, P2, P3, etc., are soil and leachate properties such as clay content, TOC, etc., supplied by the user. One set of coefficients (C1, C2, C3, etc.) was developed for each metal when it is the only solute of interest in the leachate, and another set is to be used when one or more other competing metals are present in the leachate.

The predictive equations developed from the L-A model (3) are of the form:

$$V.\# = (v/25)[C1P1 + C2P2 + C3P3 + \ldots] \quad [3]$$

where V.# is the velocity of the relative solute concentration (C/Co), e.g. # = 0.1, 0.2, 0.3, etc.; v is the pore water velocity (seepage velocity); C1, C2, C3, etc., are regression coefficients calculated from the soil column data; and P1, P2, P3, etc., are properties such as clay and iron oxide content in soil and TOC and salt concentration in leachate. There is one set of the regression coefficients for each metal and for each of 10 relative concentrations (0.1, 0.2,...0.8, 0.9). Additionally, a second set of coefficients was developed for use when one or more competing metals are present in the leachate along with the metal of interest.

The results provide a simple set of equations that can be quickly calculated without the aid of a computer. Although no field test has been conducted to date, it should be noted that the equations were based on soils with a great variety of chemical and physical properties. This suggests that the results will be broadly applicable, particularly where exact values are not of interest (as in screening studies).

Phenols Migration/Adsorption

Phenols are water contaminants both because of their toxicity and because they may, at low concentrations, render drinking water unpotable due to their strong taste and odor. Simple phenols (monohydroxybenzene derivatives) are found in soil as a result of the decomposition and disposal of organic wastes, biological synthesis, and the breakdown of aromatic pesticides. Lakes and lagoons used by paper mill industries for disposal of large amounts of delignified wood wastes contain abundant natural phenols. Oil refineries and coke plants also separate and dispose of large amounts of phenols from coal tar wastes. Industries dealing in the manufacturing and use of medicinals, dyes, resins, perfumes, explosives, disinfectants, and photodevelopers use and dispose of sizable quantities of phenols of both natural and synthetic origin.

In the phenol studies (13, 14), the parameters investigated were phenol concentration in MSW leachates versus leachate age, effect of soil composition on attenuation, and the effect of aeration.

Adsorption

Six different monohydroxybenzene derivatives (phenols) at concentrations from 5 to 200 ppm in water were mixed with small amounts of five different soil samples with which contact was maintained for up to 14 days. The amount of the various phenols adsorbed on each soil was measured, and the results were correlated with soil properties. The characteristics that correlated most highly were, in order, level of free iron oxide, pH, and percent clay.

Concentration versus Age

The natural phenol levels in Carbon dioxide-blanketed leachates ranging from 1 to 7 yr old were monitored over a 12-mo period. The phenol concentration dropped considerably in the 1-year-old (initially) leachate but remained relatively constant in 5-yr-old and 7-yr-old leachate. Even in the older leachates, the level remained at 40 to 90 times higher than that of drinking water standards, leading to the conclusion that MSW landfill leachates retained large quantities of natural phenols in solution, whether they are young or old.

Soil Composition

Anaerobic constant flux soil column experiments were run using the natural leachate as well as leachates enriched with specific phenols. The overall results showed that soils with higher iron levels were more effective at attenuating phenol migration. Also, high TOC levels and low pH in leachates correlate with low retention of phenols by soils.

Aeration

Enriched leachates were stored under carbon dioxide and also bubbled with air for 15 days. The phenol levels in the air-aerated samples were significantly reduced when compared with the levels in the carbon dioxide covered samples except for nitrophenol, which showed little reactivity.

The references listed below are reports and articles submitted in partial fulfillment of Contract 68-03-0208 and Grants R805731 and R803988 by the University of Arizona under the sponsorship of the U.S. Environmental Protection Agency. The Principal Investigator was Dr. Wallace H. Fuller of the University of Arizona, Tucson, AZ 85721. Michael H. Roulier was the EPA Project Officer.

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The NTIS order numbers are listed at the end of each reference citation. The other references were published in journals, as noted, and are available at many libraries.

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